Supporting Information for:

Mononuclear Five- and Six-Coordinate Iron Hydrazido and Hydrazine Species

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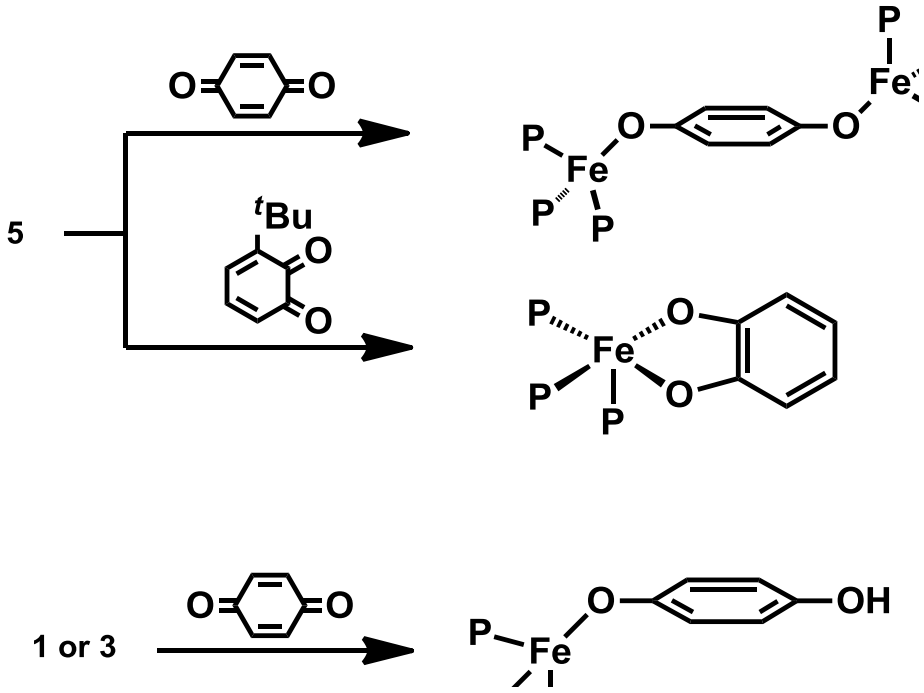
Supplementary Experimental Section

Reaction of [PhBP$^{Ph}_3$]Fe(η^2-N_2H_3) with *para*-benzoquinone. A solution of *para*-benzoquinone (0.0410 g, 0.379 mmol) in 4 mL THF was added dropwise to a solution of **5** (0.1897 mmol) in 10 mL THF at -78 ^oC. After stirring at -78 ^oC for one hour, the reaction was warmed to room temperature, and stirred an additional hour before the volatiles were removed. By ^1H NMR, several species were present. Triteration of the resulting residue with pentane, followed by THF extraction and layering of pentane afford crystals of {[PhBP$^{Ph}_3$]Fe}$_2$(μ-OArO). IR of the crude reaction mixture does not show any NH stretches.

Reaction of [PhBP$^{Ph}_3$]Fe(η^2-N_2H_3) with 3,5-ditbutyl,*ortho*-quinone. A solution of 3,5-di-^{t}butyl-*ortho*-quinone (0.0168 g, 0.0748 mmol) in 1 mL THF was added dropwise to a stirring solution of **5** (0.03741 mmol) in 3 mL THF at -78 ^oC. The reaction stirred overnight, during which it warmed to room temperature. The volatiles were removed, and the resulting solid was rinsed with pentane, extracted into THF, and filtered. The slow evaporation of pentane into the THF solution yielded purple crystals of [PhBP$^{Ph}_3$]Fe(OArO). ^1H NMR (C_6D_6, 300 MHz): δ 16.5, 11.4, 10.2, 5.9, 5.6, 4.5, 1.9, -4.2, -9.7 (bs), -9.9 (bs), -14.0 (bs). Evans Method (C_6D_6): 2.4 B.M. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 563 (5300), 820 (4170).

Reaction of [PhBP$^{mter}_3$]Fe(η^2-N_2H_3) with *para*-benzoquinone. A solution of *para*-benzoquinone (0.0027 g, 0.0246 mmol) in 2 mL benzene was added to a stirring solution of **1** (0.0246 mmol) in 2 mL benzene, and stirred for 1 h, during which the solution went from green to orange. The solution was filtered, and the volatiles were removed. The solids were extracted

into DME, and layered with pentane to afford crystals of [PhBP$^{mter}_3$]Fe(OArOH (0.0231g, 60.4 %). ^{1}H NMR (C_6D_6, 300 MHz): δ 70.1, 37.9, 19.4, 18.7, 17.4, 8.7, 7.1, 6.8, 5.5, 3.5, -8.6, -12.3, -32.5.



Scheme S1.

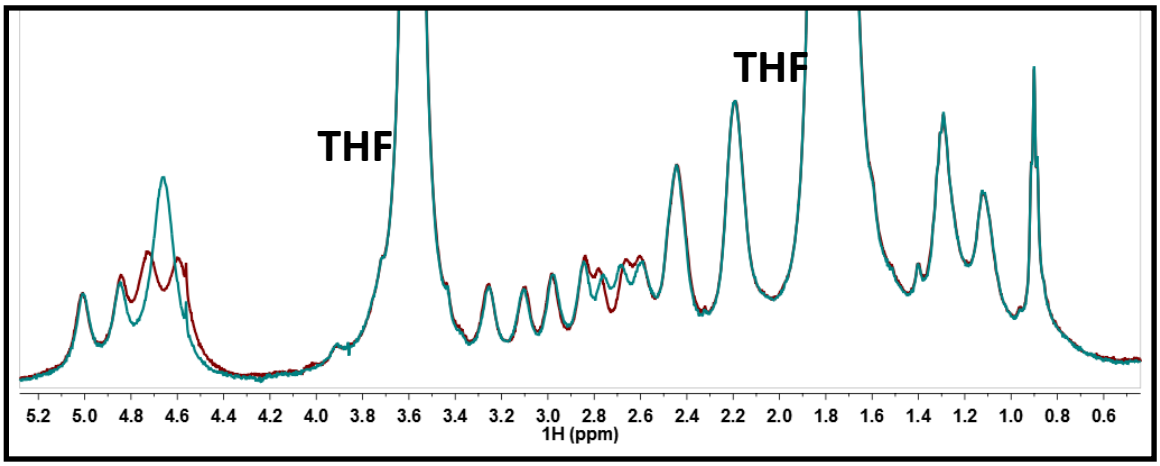


Figure S1. $^{1}H/1H\{^{15}N$, 47.4 ppm} NMR spectrum of **2** (d_8-THF, -40 ^{o}C).

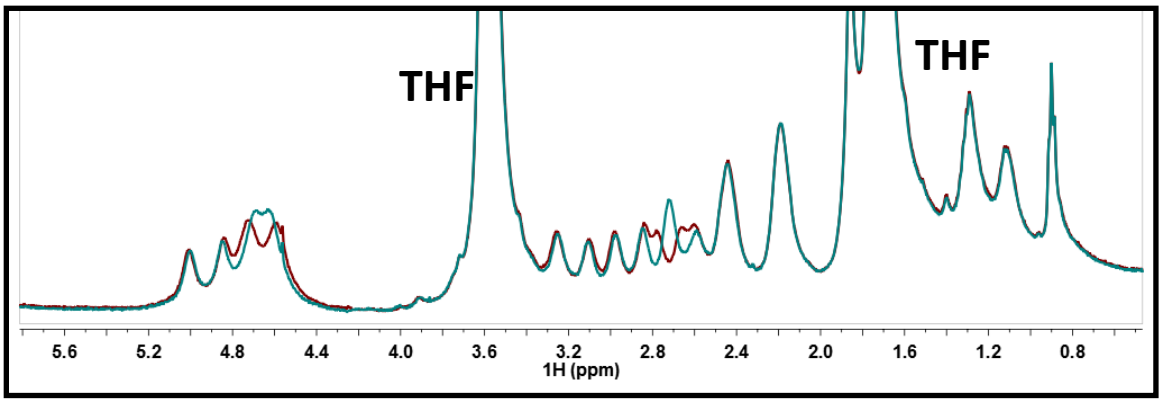


Figure S2. $^{1}H/1H\{^{15}N$, 40.8 ppm} NMR spectrum of **2** (d_8-THF, -40 ^{o}C).

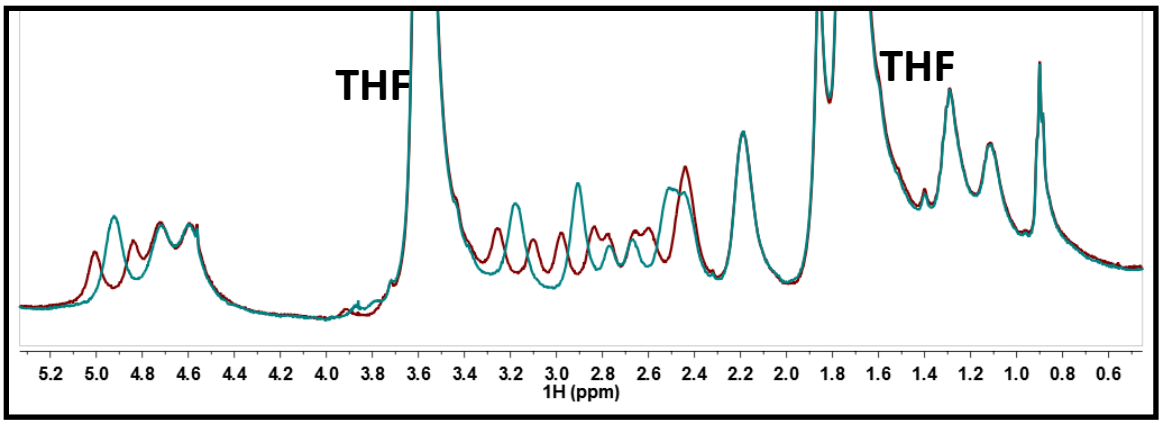


Figure S3. ^{1}H/1H{^{15}N, 23.0 ppm} NMR spectrum of **2** (d_8-THF, -40 ^{o}C).

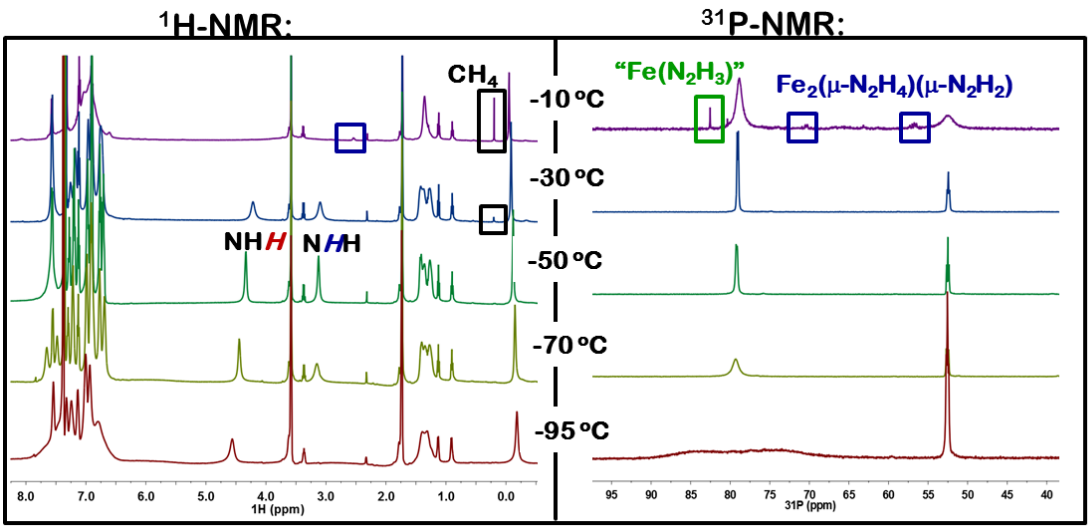


Figure S4. ^{1}H and ^{31}P NMR VT profile of **5** (d_8-THF). Peaks marked with an asterix correspond to $\{[PhBP^{Ph}_3]Fe\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_4)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2^{2-})$.

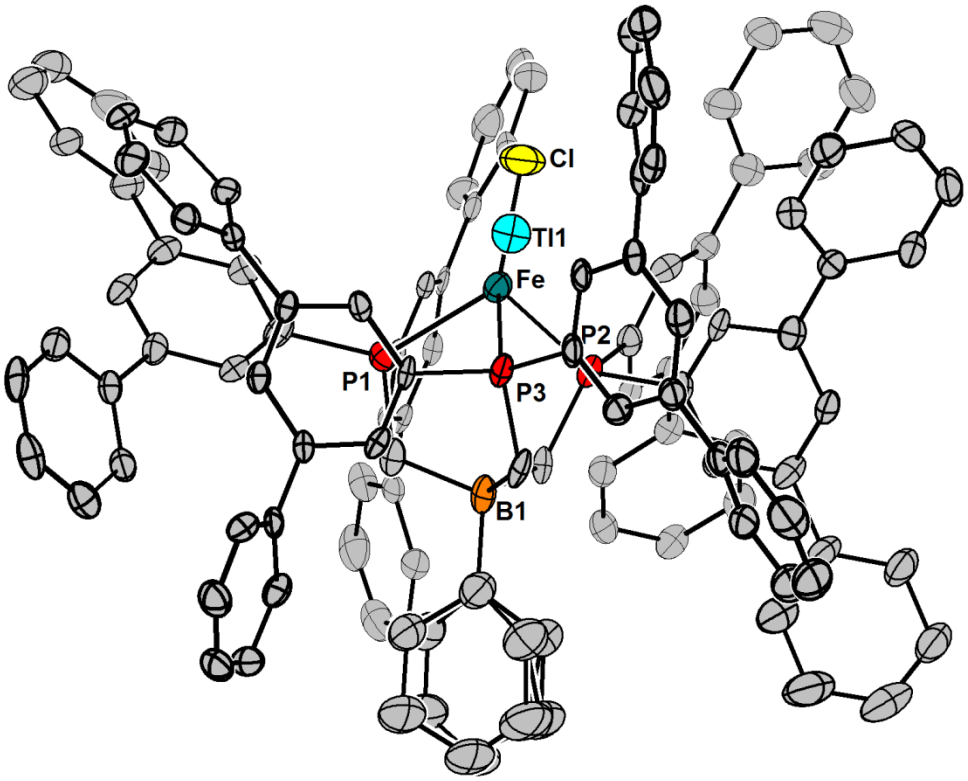


Figure S5. Solid-state structure (50% displacement ellipsoids) of [PhBP$^{m\text{ter}}_3$]FeCl, with the disordered atoms shown. Select bond lengths [Å] and angles [°] for [PhBP$^{m\text{ter}}_3$]FeCl: Fe-Cl 2.202(2), Fe-P(3) 2.408(2), Fe-P(2) 2.427(2), Fe-P(1) 2.456(2), Cl-Fe-P(3) 127.61(9), Cl-Fe-P(2) 115.54(9), P(3)-Fe-P(2) 91.21(7), Cl-Fe-P(1) 127.49(9), P(3)-Fe-P(1) 91.91(8), P(2)-Fe-P(1) 93.25(8).

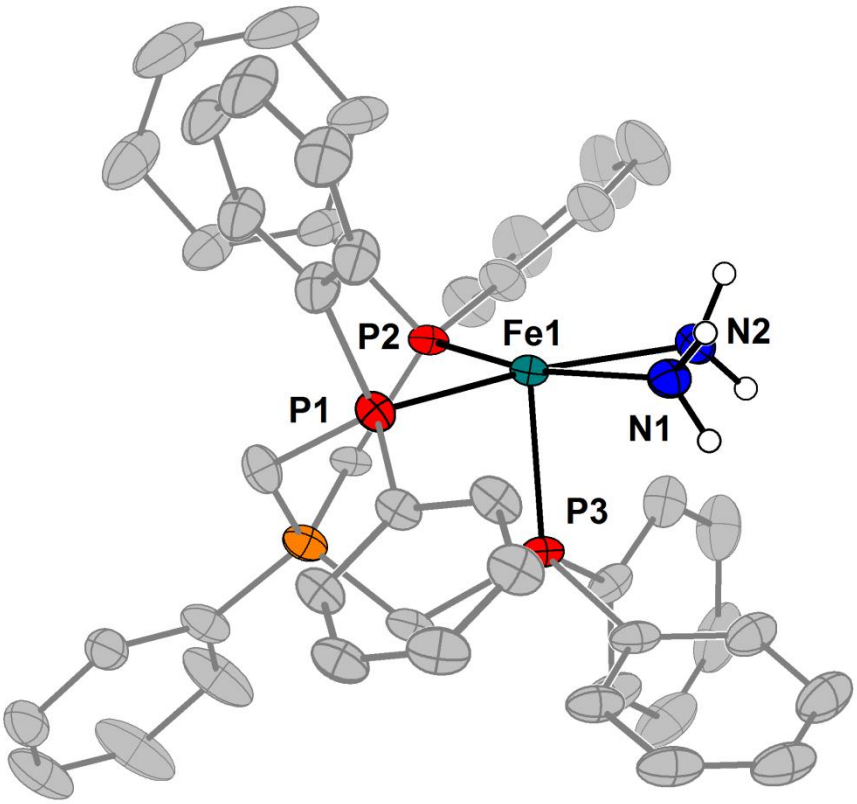


Figure S6. Solid-state structure (50% displacement ellipsoids) of the cation of {[PhBP$^{Ph}_3$]Fe(η^2-N_2H_4)}(PF_6), **7**. Hydrogen atoms, solvent molecules, the PF_6^- counteranion, and minor components of disorder have been removed for clarity. The hydrogen atoms that coordinate the hydrazine were locatd in the difference map, were refined semi-freely, and are shown.

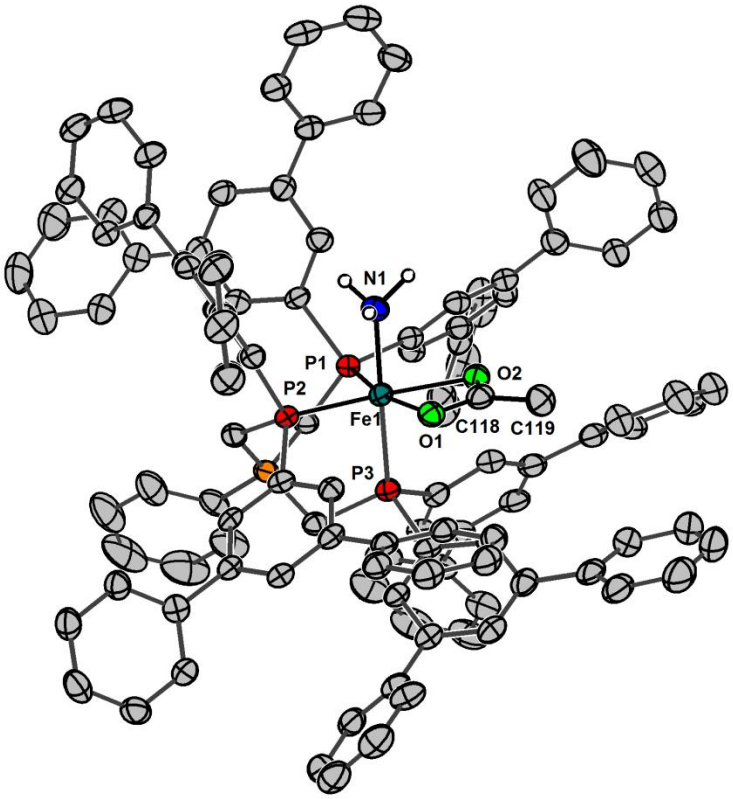


Figure S7. Solid-state structure (50% displacement ellipsoids) of [PhBP$^{mter}_3$]Fe(NH_3)(OAc), **11**. Hydrogen atoms and solvent molecules have been removed for clarity.

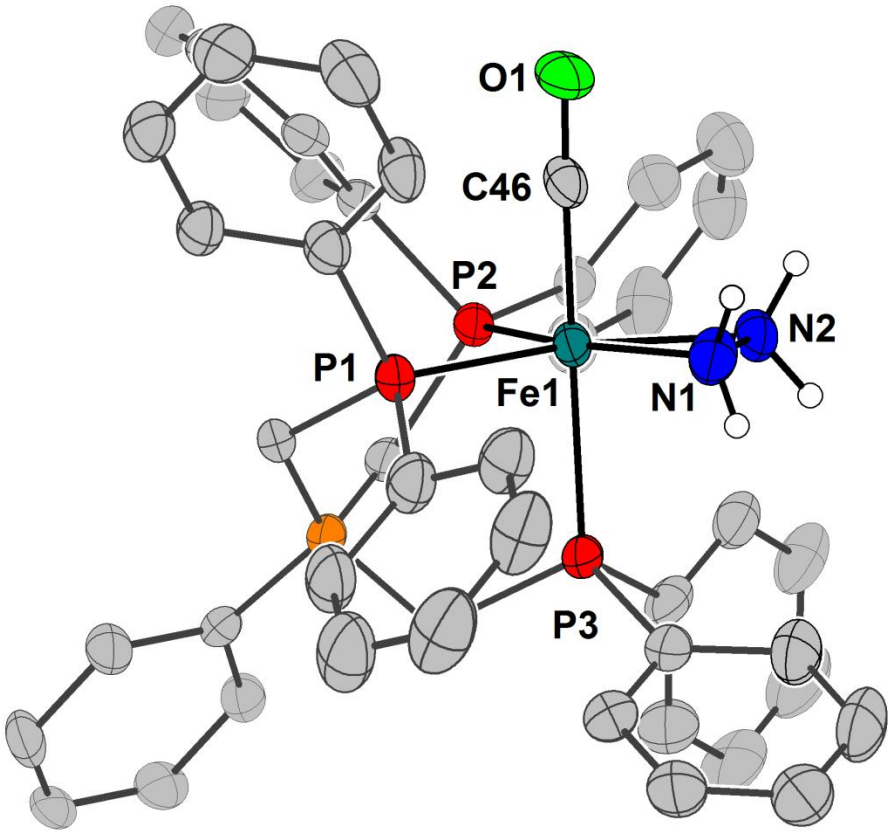


Figure S8. Solid-state structure (50% displacement ellipsoids) of the cation of {[$PhBP^{Ph}_3$]Fe(CO)(η^2-N_2H_4)}(PF_6), **13**. Hydrogen atoms, solvent molecules, the PF_6^- counteranion, and minor components of disorder have been removed for clarity. The hydrogen atoms that coordinate the hydrazine were located in the difference map, were refined semi-freely, and are shown. Select bond lengths (Å) for **12**: Fe(1)-C(46) 1.772(4),Fe(1)-N(1) 1.984(3), Fe(1)-N(2) 2.005(3).

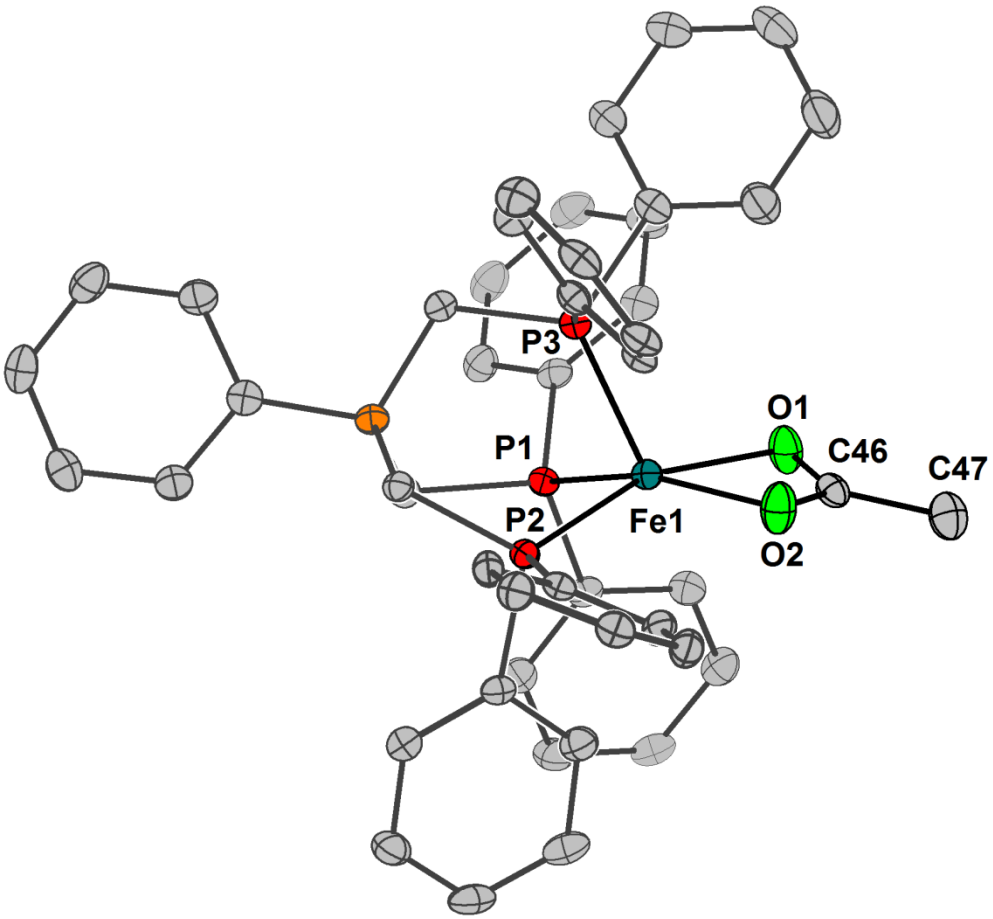


Figure S9. Solid-state structure (50% displacement ellipsoids) of [PhBP$^{Ph}_3$]Fe(OAc). Hydrogen atoms and solvent molecules have been removed for clarity.

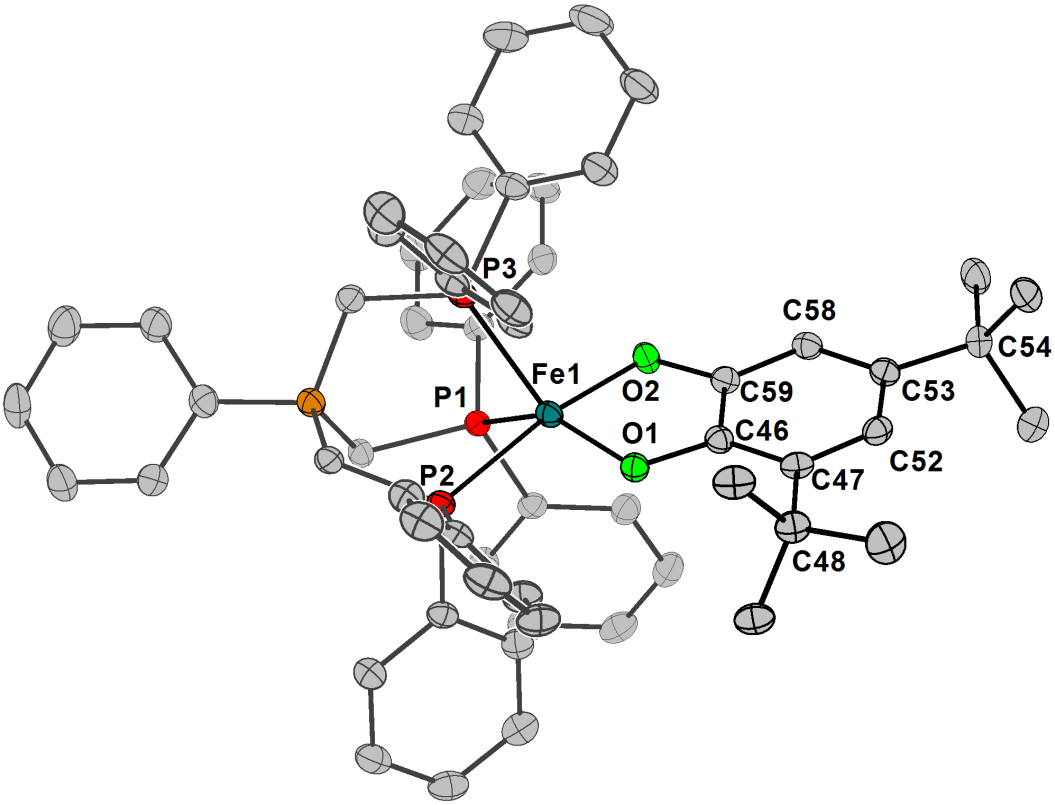


Figure S10. Solid-state structure (50% displacement ellipsoids) of [PhBP$^{Ph}_3$]Fe(κ^2-OArO). Hydrogen atoms and solvent molecules have been removed for clarity. Select bond distances (Å): Fe1-O1 1.876(2), Fe1-O2 1.856(2), Fe1-P1 2.2782(7), Fe1-P2 2.3376(7), Fe1-P3 2.2458, O1-C46 1.357(3), O2-C59 1.347(3), C46-C47 1.412(3), C47-C52 1.392(4), C52-C53 1.408(4), C53-C58 1.384(4), C59-C59 1.400(4), C59-C46 1.401(3).

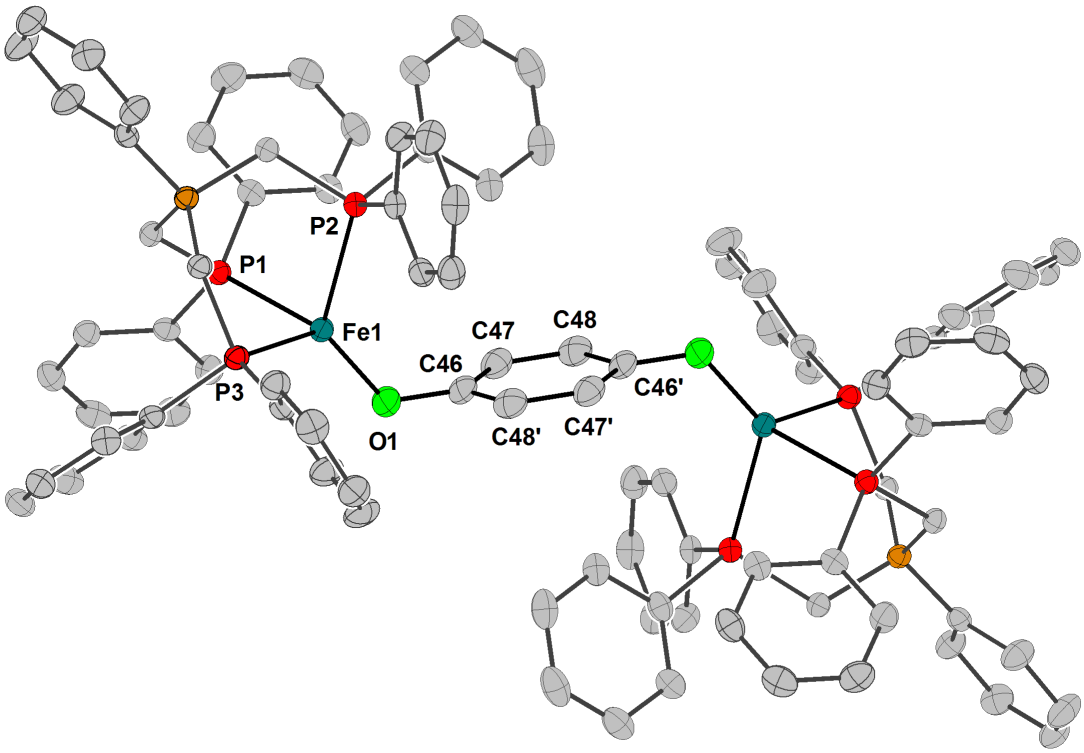


Figure S11. Solid-state structure (50% displacement ellipsoids) of {[PhBP$^{Ph}_3$]Fe}$_2$(OArO). Hydrogen atoms and solvent molecules have been removed for clarity. Select bond distances (Å) and angles (deg): Fe1-O1 1.871(2), Fe1-P1 2.4345(6), Fe1-P2 2.4573(6), Fe1-P3 2.4374(6), O1-C46 1.356(3), C46-C47 1.393(3), C47-C48 1.401(3), C46-C48' 1.391(3), Fe1-O1-C46 120.9(1), P1-Fe1-P2 91.15(2), P1-Fe1-P3 92.55(2), P2-Fe1-P3 91.69(2), P1-Fe1-O1 119.69(6), P2-Fe1-O1 128.31(5), P3-Fe1-O1 123.78(6).

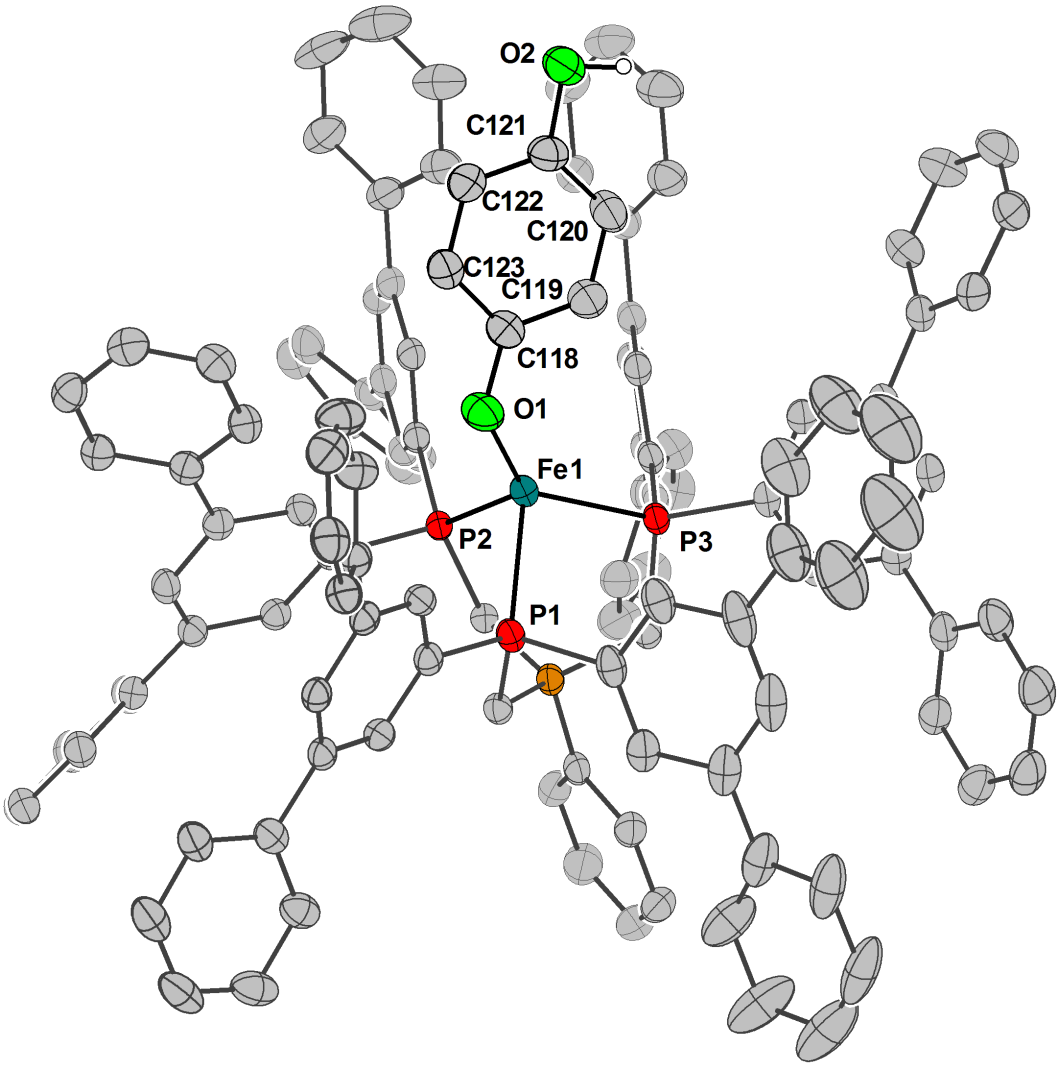


Figure S12. Solid-state structure (50% displacement ellipsoids) of [PhBP$^{mter}_{3}$]Fe(OArOH). Hydrogen atoms and solvent molecules have been removed for clarity. The acidic OH proton was located in the difference map, and is shown. Select bond distances (Å) and angles (deg): Fe1-P1 2.3966(6), Fe1-P2 2.4280(5), Fe1-P3 2.4315(5), Fe1-O1 1.858(2), O1-C118 1.327(3), C118-C119 1.393(3), C119-C120 1.395(3), C120-C121 1.382(3), C121-C122 1.383(3), C122-C123 1.377(3), C123-C118 1.401(3), C121-O2 1.380(3), P1-Fe1-P2 92.15(2), P1-Fe1-P3 95.29(2), P1-Fe1-O1 110.04(5), P2-Fe1-P3 89.84(2), P2-Fe1-O1 120.24(6), P3-Fe1-O1 138.53(5).

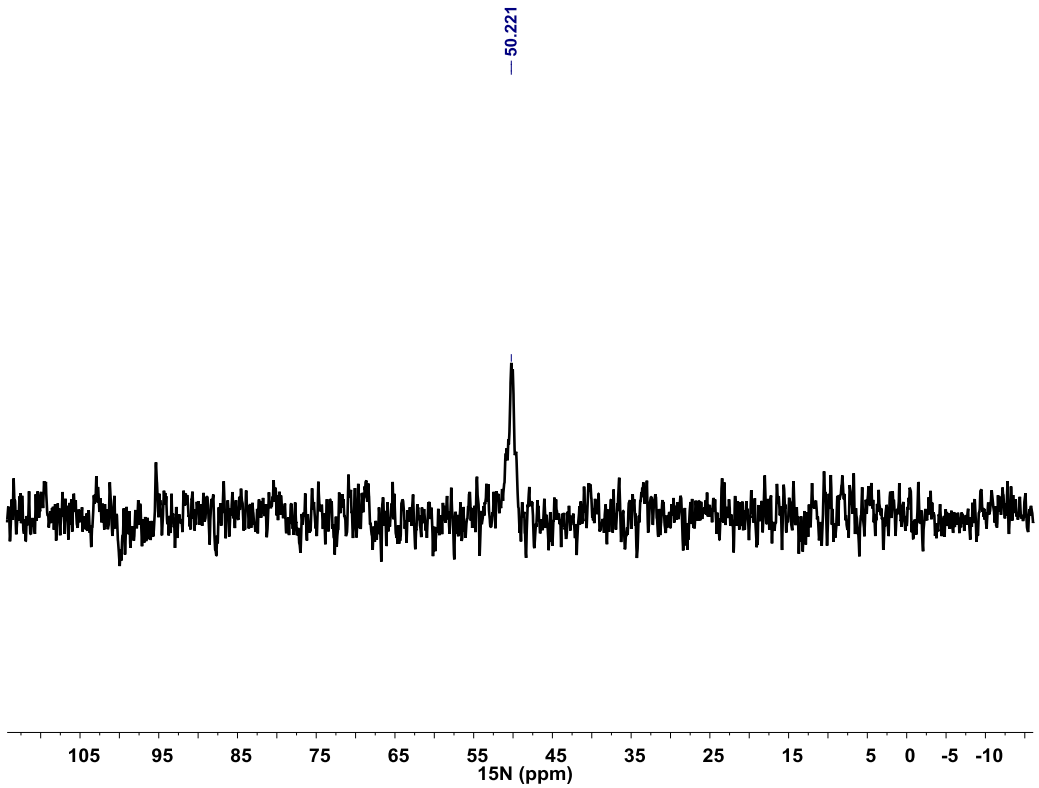


Figure S13. ^{15}N NMR spectrum of $^{15}N_2H_4$ obtained in THF-d_8 at -50 ^{o}C.